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REACTIONS IN LIQUID AMMONIA.

(Abstract.)

By EDWARD CURTIS FRANKLIN, Leland Stanford Jr. University, California.

Read (by title) before the Academy, at Topeka, December 31, 1904.

THE striking parallelism between the general properties of liquid ammonia and water has been emphasized by Franklin and his coworkers in previous papers. Water, among solvents, is characterized by its high boiling-point, its high specific heat, its high heat of volatilization, its high critical temperature and pressure, its high association in the liquid condition, its high dielectric constant, by its low boiling elevation constant, by its power to unite with salts as water of crystallization, by its wide solvent power, and by the fact that, with the possible exception of hydrocyanic acid, it is the most powerful ionizing solvent known. Aqueous solutions of salts are generally excellent conductors of electricity.

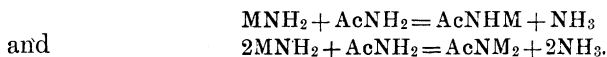
Of all well-known solvents ammonia most closely approaches water in all those properties which give the latter its unique position among solvents. While the boiling-point of liquid ammonia is thirty-three degrees below zero, it still appears abnormally high when compared with the boiling-points of such substances as methane, ethylene, hydrogen sulfide, phosphine, arsine, hydrochloric acid,¹ etc. The specific heat of liquid ammonia is greater than that of water, while its heat of volatilization, with the exception of water, is the highest of any known liquid. Its critical temperature is abnormally high, and especially the critical pressure, which is the more characteristic constant, is second only to water among solvents. Ammonia is an associated liquid, and its dielectric constant, while much below that of water, is still high. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3.4, and it quite equals water in its power to unite with salts as ammonia of crystallization. As a solvent for salts it is inferior to water, though some salts, for example, silver iodide, dissolve much more abundantly in ammonia than they do in

1. The abnormally high boiling-point of liquid hydrofluoric acid, its evident association, even in the gaseous condition, its power of uniting with fluorides, and the fact that Moissan has found a hydrofluoric acid solution of potassium fluoride to be a good conductor of electricity, have led the writer to suspect that hydrofluoric acid is to be classed with water and liquid ammonia as an electrolytic solvent.

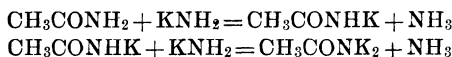
Some preliminary experiments on hydrofluoric acid have shown it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, nitrate, and chlorate, potassium bromate, acetamide, urea and potassium sulfate are abundantly soluble; silver cyanide, barium fluoride and copper chloride appear to dissolve to some extent; while calcium fluoride, copper sulfate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride and metallic magnesium are insoluble.

water, and it far surpasses this solvent in its power to dissolve the compounds of carbon. Finally, it exhibits very marked power as an ionizing solvent. The more dilute ammonia solutions are much better conductors than aqueous solutions of equal concentration.

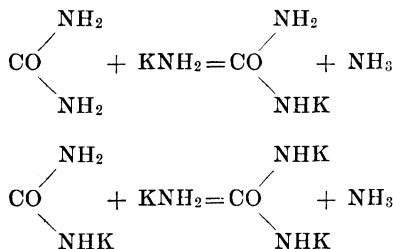
Metallic Derivatives of the Acid Amides, Compounds Related to Ammonia as the Ordinary Metallic Salts are to Water. ("Ammonsalts," "Amidesalts," "Acidamidesalts." Suggest a good name.) In view of the close general resemblance between ammonia and water, the writer, collaborating with Mr. O. F. Stafford, was led to study the reactions between acid and basic amides in ammonia solution. The result of this work was to show that these substances behave in ammonia in a manner entirely analogous to the action of acids and bases in water. Franklin and Stafford have shown that the acid amides, which discharge the red color of a solution of phenolphthaleine in ammonia, react with the soluble basic amides, which give the characteristic red color with the same indicator, to form metallic derivatives of the acid amides, in accordance with the following general equations:



Acetamide and potassium amide, for example, react with each other as follows:

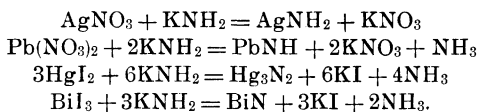


Carbamide and potassium amide, as follows:



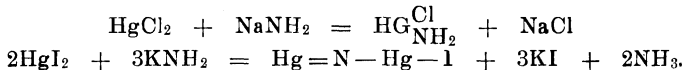
Metallic Amides, Imides, and Nitrides. (Basic Amides, Basic Imides. "Ammon Bases.") Continuing in the direction suggested by the above-outlined analogy between water and ammonia, the writer now finds that the soluble basic amides react with the salts of the heavy metals in solution in ammonia to form amides, imides or nitrides of the heavy metals. For example, potassium amide reacts with silver nitrate to form silver amide, with lead nitrate to form lead imide, and with mercuric iodide and bismuth iodide to form mercury

nitride and bismuth nitride, respectively. The reactions are represented by the following equations:



These substances are precipitated when potassium amide and the salts are brought together in ammonia solution. Silver amide is pure white, lead imide is orange, bismuth nitride is dark brown, and mercury nitride is chocolate brown. All of these compounds are very explosive. So sensitive, indeed, is silver amide that only with great difficulty was the analysis of the compound accomplished.

Compounds Related to Ammonia as the Ordinary Basic Salts Are to Water. ("Ammonbasic Salts," "Basic Amide Salts." Suggest a good name.) In some cases when the metallic salt is in excess, the result of the action of the alkali amide on the salt is a compound related to ammonia as the ordinary basic salts are to water. Examples of these compounds are HgClNH_2 , $\text{Hg}=\text{N}-\text{Hg}-\text{Br}$ and $\text{Hg}=\text{NHg}-\text{I}$, which are formed when mercuric chloride, bromide, and iodide, respectively, are treated with potassium amide. The reactions take place in accordance with the equations:

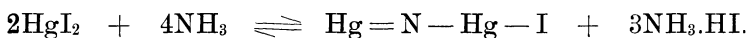


HgClNH_2 is the well-known infusible white precipitate, which is usually considered to be mercuriammonium chloride, $\text{Hg}=\text{NH}_2\cdot\text{Cl}$, but by the writer looked upon as a compound related to ammonia as a basic salt is to water, with the formula given above. This formula, originally proposed for mercury chloramide by Kane some sixty years ago, has, in recent years, been discredited on the authority of Rammelsberg. The other two compounds are less well known. They are described in the literature as having been prepared from aqueous solutions, while their existence has also been denied. According to Rammelsberg, they are dimercurammonium salts; the iodide, for example, having the formula $\text{Hg}\equiv\text{N.I}$. The author's formulation is given above. These basic compounds dissolve in liquid ammonia solutions of ammonium salts, in a manner analogous to their solution in dilute aqueous acids, as indicated by the equation



Phenomena in Liquid Ammonia Analogous to Hydrolysis in Water. ("Ammonolysis," "Amidolysis," "Ammolysis." Suggest a good name.) The salts of mercury, arsenic, antimony, tin, aluminum and probably salts of other metals react with pure dry liquid ammonia in a manner analogous to ordinary hydrolytic action in water.

For example, mercuric choride gives a small amount of mercury chlor-amide, and mercuric iodide gives $\text{Hg}=\text{N}-\text{Hg}-\text{I}$, both of which dissolve in excess of ammonium salts. Bismuth nitrate¹ and aluminum iodide give white precipitates of their respective basic salts, both of which are soluble in ammonium salts. The reversible equation representing the action of ammonia on mercury iodide is given.



The Mercury Ammonium Bases. In the light of the above outlined relations, it would seem that certain of the so-called mercury ammonium bases are to be looked upon as mixed compounds containing residues basic to both ammonia and water, while others are simply mercury salts with ammonia of crystallization. For example, the fusible white precipitate is to be formulated $\text{HgCl}_2\cdot 2\text{NH}_3$, and not as a double salt of mercury ammonium iodide and ammonium iodide, $\text{Hg}=\text{NH}_2\text{I}\cdot\text{NH}_4\text{I}$, nor as the double salt of dimercurammonium iodide and ammonium iodide, $\text{Hg}_2\text{NI}\cdot 3\text{NH}_4\text{I}$, nor yet as mercury diammonium diiodide, $\text{Hg}(\text{NH}_3)_2\text{I}_2$, although it may be that the latter formula represents the manner in which ammonia of crystallization associates itself with the salt.

The chloride of Millon's base, instead of being oxydimercurammonium chloride, $\text{O}\begin{smallmatrix} \text{Hg} \\ \diagup \quad \diagdown \\ \text{Hg} \end{smallmatrix} \text{NH}_2\cdot\text{Cl}$, or dimercurammonium chloride with water of crystallization, $\text{N}(\text{Hg}_2)\text{Cl}\cdot\text{H}_2\text{O}$, is better formulated as a compound or mixture of salts basic to ammonia with salts basic to water. Of the half-dozen or more possible formulas, the following are given: $\text{HgO}\cdot\text{HgClNH}_2$; $\text{NH}_2-\text{Hg}-\text{O}-\text{Hg}-\text{Cl}$; $2\text{HgO}\cdot\text{Hg}(\text{NH}_2)_2\cdot\text{HgCl}_2$.

Compounds Related to Ammonia, as the Plumbates, Aluminates, etc., are to Water. Certain metallic amides, the lead and aluminum derivatives, for example, dissolve in excess of potassium amide, just as metallic hydroxides and oxides dissolve in potassium hydroxide, forming compounds presumably of the type PbNK or $\text{Pb}(\text{NHK})_2$. Several amides have been found to dissolve in this way, but so far only in the case of the lead compound has the attempt been made to isolate and analyze the salt formed. The analysis indicates the compound PbNK , but the difficulty of separating the pure substance from the other products of the reaction has thus far rendered attempts to obtain concordant analyses futile.

1. Not the ordinary salt with water of crystallization, but the salt formed electrolytically at a bismuth electrode in ammonia solution.

NOTE.—One further matter deserves mention, namely, a new instance of the catalytic action of platinum and certain metallic oxides. The potassium amide used in the above-described experiments is made by the action of liquid ammonia on metallic potassium. The action is a slow one, a fraction of a gram of metallic potassium, with large excess of ammonia, being completely converted into potassium amide only after the lapse of days. The writer finds that the presence of spongy platinum or of the oxide of iron greatly accelerates the reaction. The addition of a very small quantity of spongy platinum brings the action to completion in the course of about fifteen minutes.